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## Optical spectroscopy of quantum spin systems

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# Summary

This thesis work illustrates the results obtained on a number of solid crystalline materials using optical spectroscopy. This experimental technique consists of shining light of different frequencies onto the sample under investigation, and of observing which frequencies are absorbed by the material itself. The experiments were performed in the frequency range extending from the far infrared to the ultra violet (i.e., from 4 meV to 4 eV). Linearly polarized light was used, therefore characterized by a well defined direction of oscillation for the electric field of the radiation, in order to probe the possible anisotropy of the samples. In this way we could investigate the lattice vibrational modes (detectable in a solid in the far-infrared region), and the electronic and/or magnetic excitation spectra. Additional information was obtained by performing the optical experiments while varying the temperature of the samples between 4 and 300 K. From the detailed analysis of the temperature dependent experimental data, we could learn about the crystal structure of the different systems, and their electronic and magnetic properties like, e.g., ground state configuration, electron-phonon coupling, and spin-charge interplay.

As far as the compounds discussed in this thesis are concerned (transition metal monosilicides,  $\text{CuGeO}_3$ , and  $\alpha'\text{-NaV}_2\text{O}_5$ ), the common feature is that they all belong to the class of *strongly correlated electron systems*, i.e., compounds whose properties are dominated by strong electron-electron correlations. This is the case when the on-site electron-electron repulsion  $U$  is much larger than the energies associated with the overlap of atomic orbitals belonging to different atoms. Because these energies are characterized, in a solid, by the width  $W$  of the energy band under consideration, a large  $U/W$  ratio is expected in systems involving well-localized electrons like the  $4f$  and  $5f$  electrons of the rare earths and the actinides, respectively, but also the  $d$  electrons of the transition metals (TM).

The importance of electron-electron correlations in influencing the basic properties of a compound can be understood considering the example of  $\text{CoO}$ . This oxide, if treated within the independent-electron approximation (i.e., writing the total wavefunction of the  $N$ -electron system in the form of an antisymmetrized product of single-electron wavefunctions), is expected to be metallic, with an odd number of electrons per unit cell and a partially filled  $d$  band. In reality, as a consequence of strong correlations, which are suppressing charge fluctuations and therefore the electrical conductivity,  $\text{CoO}$  is an insulator.

More in general, strong electron-electron correlations can give rise to a large variety of peculiar phenomena, the most famous being probably high-temperature superconductivity, heavy-fermion and Kondo-insulating behavior, and colossal magnetoresistance. For

the description of these collective phenomena, and for the development of appropriate microscopic models, it is useful to investigate the elementary excitations of these materials. In fact, the excitations between the ground state and the lowest excited states reflect the interplay between quantum magnetism and low energy charge degrees of freedom, a fingerprint of strong electron-electron correlations.

In the course of this thesis work we investigated a number of TM mono-silicides and, among them, in particular FeSi which shows Kondo-insulating behavior at low temperature. Moreover, we studied quasi-one-dimensional (1D) systems in which electron-electron correlations, together with the low dimensionality, give rise to fascinating phenomena like the spin-Peierls (SP) phase transition ( $\text{CuGeO}_3$ ), and the direct optical absorption for spin-flip excitations ( $\alpha'$ - $\text{NaV}_2\text{O}_5$ ).

### Infrared Spectroscopy Study of Phonons Coupled to Charge Excitations in FeSi

We investigated the optical response of FeSi, CoSi, and MnSi. Whereas on CoSi and MnSi we observed a metallic behavior at any temperature, on FeSi we could follow the opening of a gap of the order of 70 meV, upon reducing the temperature below 100 K.

By analyzing in detail the phonon spectra we could determine the dynamical (or transverse effective) charge of the TM atoms and Si, for each temperature: The large value  $e_T^* \approx 4e$  was obtained on all compounds. For a purely ionic insulator this is also the actual charge of the ions. However, because the TM atoms and Si have practically the same electronegativity and electron affinity, strong ionicity is not expected from a chemical point of view in this class of materials. On the other hand, for a covalent compound with resonating bonds a finite value of the transverse effective charge results from a dynamical charge redistribution associated with the ionic motion due to an optical phonon. We showed that the large value of the transverse effective charge, along with the resonance behavior of the phonon parameters, observed on FeSi when the gap sweeps through the phonon-frequency, provides strong evidence for a moderate coupling between the vibrational degrees of freedom and low energy electron-hole excitations in these systems ( $\lambda \approx 0.1$ , in FeSi).

Based on the discussion of the infrared spectra presented in this thesis and of published transport data, we provided a qualitative model for the electronic structure of the TM mono-silicides. The main conclusion is that six electrons per transition metal atom are engaged in chemical bonds to the Si sublattice. The remaining electrons of the TM atoms (e.g., two for FeSi) occupy a doubly degenerate quasi-atomic  $d$ -state, and obey Hund's rules: In FeSi, the two localized  $d$  electrons result in a local moment  $S = 1$  on the Fe site. The conduction band supports two weakly bound itinerant electrons (mainly of Si  $3p$  character) which in the case of FeSi, at sufficiently low temperatures, compensate the local moment losing their itinerant character, by forming what is called a Kondo singlet ( $S = 0$ ). This framework provides a basis for understanding the observed range of chemical stability of these compounds (from CrSi to NiSi), and the physical properties of FeSi.

## Infrared Signatures of the Spin-Peierls Transition in $\text{CuGeO}_3$

$\text{CuGeO}_3$  is considered as a quasi-1D system because weakly-coupled 1D  $\text{CuO}_2$  chains, running parallel to each other, can be identified in this material. Each  $\text{Cu}^{2+}$  ion is in a  $d^9$  electronic configuration which corresponds to a spin  $S = 1/2$  on each Cu site. These magnetic moments interact antiferromagnetically: For each spin it is more favorable to be antiparallel (rather than parallel) with respect to the two neighboring spins.

In 1993,  $\text{CuGeO}_3$  was recognized as the first inorganic compound showing a SP phase transition: A lattice distortion that occurs together with the formation of a nonmagnetic ground state ( $S = 0$ ), and the opening of a finite energy gap in the magnetic excitation spectrum. This magneto-elastic transition is driven by the magnetic energy gain due to dimerization of the antiferromagnetic exchange between the spin  $1/2$  moments of the  $\text{Cu}^{2+}$  ions, which overcompensates the elastic energy loss resulting from the deformation of the lattice. In the SP ordered phase (i.e., for  $T < T_{\text{SP}} = 14$  K), the  $\text{Cu}^{2+}$  magnetic moments form singlet dimers along the chains, and spin triplet excitations are gapped.

Because the phase transition involves a lattice distortion and, therefore, a change of the symmetry of the crystal, the phonon spectrum is expected to change across the transition. Therefore, we have been investigating the temperature dependent optical spectra of pure and doped  $\text{CuGeO}_3$  concentrating, in particular, on the lattice vibrational modes. As a matter of fact, we could detect new optical phonon modes activated by the SP phase transition, and reflecting the lower symmetry of the system for  $T < T_{\text{SP}}$ . Following the temperature dependence of these modes we were able to determine the second order character of the phase transition and to study the effect of doping on  $T_{\text{SP}}$ : In particular, we showed that the substitution of Ge with Si is three times more efficient, than the one of Cu with Mg, in reducing  $T_{\text{SP}}$ . This result was discussed in relation to the difference, between Mg and Si doping, in affecting the magnetism of the system.

Furthermore, we detected a direct singlet-triplet excitation, across the magnetic gap, which is in principle optically forbidden on the basis of the crystal structure generally assumed, for  $\text{CuGeO}_3$ , in the high temperature phase. The optical activity of this excitation and the strong changes observed in the phonon spectra of Si-substituted samples might be explained in terms of an alternative crystal structure, recently proposed for  $\text{CuGeO}_3$ .

## Direct Two-Magnon Optical Absorption in $\alpha'\text{-NaV}_2\text{O}_5$ : “Charged” Magnons

After  $\text{CuGeO}_3$ , another inorganic compound,  $\alpha'\text{-NaV}_2\text{O}_5$ , has been attracting the attention of the scientific community working on low-dimensional spin systems, in general, and on the SP phenomenon, in particular. In fact, in 1996 the SP picture was proposed to explain the low temperature properties of  $\alpha'\text{-NaV}_2\text{O}_5$ , with a transition temperature  $T_{\text{SP}} = 34$  K. The basic building blocks of the crystal structure are linear chains of alternating V and O ions. These chains are grouped into sets of two, resulting in a two-leg ladder with rungs formed by two V ions, one on each leg of the ladder, bridged by an oxygen ion. Only one V  $d$  electron per rung is present (i.e.,  $S = 1/2$ ). Because the coupling between the ladders is weak, also  $\alpha'\text{-NaV}_2\text{O}_5$  has a quasi-1D character.

As in the case of  $\text{CuGeO}_3$ , by analyzing the optically allowed phonons at various temperatures below and above the phase transition, we concluded that a second-order change to a larger unit cell takes place below 34 K, as expected for a SP transition. On the other hand, on the basis of specific heat measurements in high magnetic field recently reported, the interpretation of the phase transition in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  is still controversial. In particular, the reduction of  $T_{\text{SP}}$  upon increasing the intensity of the externally applied magnetic field, which is typical for a true SP system, has not been observed.

This already quite puzzling picture became even more complicated when the crystal structure and the symmetry of the electronic configuration of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , in the high temperature phase, were investigated in detail. In fact, on the basis of x-ray diffraction measurements we found, in agreement with other groups, that the symmetry of this compound at room temperature is better described by the centrosymmetric space group  $Pm\bar{m}n$  than by the originally proposed  $P2_1mn$ . On the other hand, the intensities and polarization dependence of the electronic excitations detected in our optical spectra were not understandable in terms of a centrosymmetric space group.

We showed that a consistent interpretation of both x-ray diffraction results and optical conductivity data requires a charge disproportionated electronic ground-state, at least on a local scale, i.e., an asymmetrical charge distribution of the V  $d$  electron on each rung, without any long range order. We found that the presence of only one V  $d$  electron per rung, along with the broken left-right parity of the ground-state, gives rise to a fascinating behavior of the spin flips in  $\alpha'$ - $\text{NaV}_2\text{O}_5$ : Spin-flip excitations carry a finite electric dipole moment, which is responsible for the detection of *charged bi-magnons* in the optical spectra, i.e., direct two-magnon optical absorption processes.

Finally, we discussed the relevance of these findings to other quasi 1D and quasi 2D strongly correlated electron systems, where the interplay of spin and charge plays a crucial role in determining the low energy electrodynamics. The possibility to observe bi-magnon excitations directly, in optical spectroscopy, may become extremely useful in the study of, e.g., magnetic excitations near defects and phase-antiphase boundaries. Moreover, we expect that further study of this effect in other materials will provide important clues to the notorious mid-infrared bands in many doped strongly correlated antiferromagnetic materials, such as the high-temperature superconductors.